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# MOLECULAR COLLISION PROCESSES IN GASES AND AT SURFACES

Interim Scientific Report for Year Ending 2/28/85

*Final*

AFOSR Grant F49620-C-84-0038

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## Introduction

Our research centers on the use of Fourier Transform Infrared Spectrometry (FTIS) to determine the distribution of rotational and vibrational energies in molecules. Our particular concern is with the effects of gas-gas and gas-surface collisions on these internal states. By studying the changes in energy and structure that occur during such collisions we aim to elucidate the kinetics and dynamics of the reactive and inelastic scattering events that play leading roles in many important processes of both technological and scientific interest. The collision processes under study are brought about with the aid of supersonic free jets expanding into vacuum from small sonic orifices or nozzles. Three kinds of scenarios are used: (1) Single Free Jets. The jet itself is the stage for collisions that occur while the gas is expanding from stagnation pressure in the source to the background pressure in the vacuum chamber which is always low enough so that the jet gas is in free molecule (collisionless) flow in its terminal state. Because the expansion rates are so rapid the terminal gas state is usually far from equilibrium. Spectroscopic interrogation of jet gas allows us to characterize the nature of the collision processes that lead to the terminal state. (2) Colliding Jets. Two jets intersect at axial distances sufficiently large to insure that each jet is well into the free molecule flow regime so that molecules from one jet undergo single collisions with molecules from the other. The object in this configuration is to study the consequences of gas-gas encounters. In particular, we have been concerned with the cross-sections for translation-vibration (TV) excitation of molecules that radiate in the infrared when they are vibrationally excited. (3) Jet-Surface Combinations. In

this configuration the jet flux impinges upon a surface in the free molecular regime of the flow field so that the spectrometrically observed changes in molecular internal energy are due to single surface collisions.

These various combinations of free jets, surface and infrared radiometry-spectrometry have made possible a number of important results. Noteworthy among them are: (1) Determination of Translation-Vibration (TV) excitation cross-sections for  $\text{CO}_2$  in collisions with  $\text{H}_2$ ,  $\text{N}_2$ , Ar and  $\text{O}_2$  at relative velocities up to 6 km/s. (2) Determination of the distribution of rotational energy in TV excited  $\text{CO}_2$ . (3) Determination of excitation probabilities for rotational and vibrational degrees of freedom during collisions between CO, NO and  $\text{CO}_2$  and hot metal surfaces. (4) Elucidation of the distribution of activation energy among the various degrees of freedom in nascent  $\text{CO}_2$  molecules formed during the oxidation of CO on platinum surfaces. (5) Determination of the effect of surface coverage on energy distribution in nascent product molecules from the surface catalyzed oxidation of Co by time-resolved FTIS measurements. (6) Elucidation of some mechanistic details of the oxidation of C atoms by O atoms on a platinum surface by FTIS analysis of product CO molecules. (7) Measurements of terminal distributions of internal energy in free jet molecules to determine rotational relaxation rates in  $\text{CO}_2$ .

#### Progress During the Grant Year

1. Single Free Jets. We have continued our studies of terminal rotational distributions in both emission and absorption for  $\text{CO}_2$ , CO and mixtures of these species with  $\text{N}_2$ , Ar and He. It emerges that diluting with these gases, particularly Ar and He, increases the departure from a Boltzmann distribution. It seems possible to explain these observations in terms of a competition between de-Boltzmannizing RT transfers and Boltzmannizing RR transfers. These results are among the very few which show the importance of RR transfers in the rotational

relaxation of polyatomic gases. A paper describing these studies has been published in the Proceedings of the 14th International Symposium on Rarefied Gas Dynamics.

Our ability to determine terminal internal energy distributions in free jet expansions by emission spectrometry stems from the fact that emitting vibrational modes in many molecules do not relax appreciably during free jet expansion because of the limited number of collisions. Clearly, these modes must be excited in the source gas if they are to radiate after the expansion is over. We have depended upon thermal excitation which obviously requires elevated source temperatures. In the hope that we could achieve such excitation at low source temperatures we have recently tried maintaining a DC corona discharge in the source gas. Preliminary experiments with  $\text{CO}_2$  and  $\text{CO}$ , neat or in admixture with  $\text{N}_2$  or  $\text{He}$ , have provided some fascinating spectra rich in a variety of features that invite further exploration and examination. In particular, we have found that much lower terminal rotational temperatures can be achieved because of the lower source temperature. The resulting narrowing of the rotational spread makes it possible to resolve the combination bands involving the bending modes in  $\text{CO}_2$ . We find that these modes seem to relax during expansion so we can hope to determine their characteristic relaxation rates. Moreover, some new lines appear in the  $\text{CO}_2$  spectrum forming what seem to be R and P branches about 70 wave numbers to the red side of the asymmetric stretch  $v = 1$  band. We have identified this new band as being due to radiation from the asymmetric stretch mode of  $^{13}\text{CO}_2$ . The intensity is about 15 per cent of that from the  $^{12}\text{CO}_2$  band although the natural abundance of  $^{13}\text{C}$  is only 0.01 that of  $^{12}\text{C}$ . Although it is tempting to conclude that we have stumbled upon a remarkable isotope enrichment phenomenon we believe the following explanation is more reasonable. A vibrationally excited  $^{12}\text{CO}_2$  encounters a ground state  $^{13}\text{CO}_2$  and transfers a quantum of asymmetric stretch vibrational energy. The excess  $70\text{ cm}^{-1}$  is taken up in rotation of both

partners. Because the rotational temperature is low, the population of high  $J$  levels is so low that the vibrationally excited  $^{13}\text{CO}_2$  does not encounter a  $^{12}\text{CO}_2$  in a sufficiently high  $J$  level to act as a partner for the reverse reaction. Thus the vibrational energy remains trapped in the  $^{13}\text{CO}_2$ . These results are the basis for a paper in preparation.

2. Colliding Jets. The principal activity has been the development of a gas dynamic method of modulating or chopping the free jet. In our original TV excitation experiments we achieved the necessary sensitivity by measuring total radiation (not spectrally resolved) from collisionally excited species. We took advantage of phase-sensitive detection at imposed frequencies by mechanically chopping one of the jets with a rotating wheel. A major source of noise was due to reflection of photons from the heated nozzle by the chopping wheel. In some recent experiments we have been able to modulate the free jet successfully by using a small auxiliary pulsed jet that intersects the primary jet at right angles to its axis near the nozzle exit. In effect, the primary jet is "blown" out of the collision region and field of view when the auxiliary jet is on. As long as the pulsing gas is transparent to infrared there is no spurious signal to be seen by the detector. The marked reduction in noise has made it possible to obtain useful signals at much lower source temperatures than were possible with the mechanical chopper. Indeed, we have finally obtained clean signals with water vapor jets, an objective that has long eluded us.

3. Jet Surface Studies. We have continued our time resolved studies of surface scattered species, in particular the effect of surface coverage on rotational energy distribution in nascent  $\text{CO}_2$  molecules formed by the surface catalyzed oxidation of CO by  $\text{O}_2$ . It is very difficult to vary surface coverage over an appreciable range in a steady state experiment without a wide variation in surface temperature. With a pulsed nozzle we can achieve very high instantaneous fluxes that flood the surface.

We have also observed an emission continuum from species formed when O atoms react with CO chemisorbed on a Pt surface. A possible explanation attributes this radiation to CO<sub>2</sub> molecules preferentially excited to the  $v = 9$  level. These excited CO<sub>2</sub> molecules apparently can react with O atoms to form excited O<sub>2</sub> and CO excited to the  $v = 1$  level. These observations have been described in a note in Chem. Phys. Lett.

#### Cumulative Publication List

"Flowfield Calculations in Nonequilibrium Free Jets by the Method of Characteristics," M. Labowsky, S. B. Ryali, J. B. Fenn and D. R. Miller in Rarefied Gas Dynamics (S. S. Fisher, ed.) Prog. in Astro. and Aero. 74, 695 AIAA (1981).

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#### Personnel

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